

phases is added to the melt. Melt drops are then formed and allowed to cool and solidify during up to 70 seconds, preferably 20-70 seconds. It is preferred to use a cooling belt for
5 solidification of the particles. The belt is cooled by air, water, oil or another medium.

The melt temperature is preferably kept 0-10°C below the crystallization point of the melt. When calcium nitrate particles are produced, $\text{CN} \cdot 2\text{H}_2\text{O}$ and $\text{CN} \cdot 3\text{H}_2\text{O}$ are used as seed
10 particles. The particles formed have a particle size between 0,2 and 0,8 mm, preferably between 0,4 and 0,6 mm. Particles could be made from a melt consisting of 74 weight % calcium nitrate, 14 weight % potassium nitrate and 12 weight % water. Solid particles can also be produced consisting of a homogenous mixture of nitrates, chlorides and crystal
15 water. An example of this is particles made from a melt consisting essentially of 50 weight % calcium nitrate, 4 weight % ammonium nitrate, 26.5 weight % calcium chloride and 18-20 weight % water.

Several experiments were carried out in order to try to make particles of the melts.

Example 1 - Granules

20 CN-water solutions were evaporated to above 70, 75 and 78 weight % CN .

The various melts were sprayed onto a rotating laboratory pan granulator containing solid NH-CN (calcium nitrate from Norsk Hydro ASA) in various ratios and at various temperatures.

25 None of the trials succeeded as the liquid/melt did not solidify. The whole matrix (solid CN+melt) turned into a sticky slurry that could not be processed with liquid/solid ratios within acceptable limits

Example 2 - Prills

30 Melts with the CN concentrations mentioned above, were kept at temperatures close to the crystallization point given by the literature. Finely crushed NH-CN were mixed into the melt subsequent to pumping the melt at high pressure to nozzles where drops were formed and allowed to cool down to 20°C for 5-10 seconds.

As cooling medium oil and air were tried. Solid particles did not form due to under-cooling.

5 **Example 3 - Making pastilles**

Trial 1:

Droplets of CN-melts with CN concentrations above 70, 75 and 78 weight % pure CN where allowed to cool on a chilled metal plate down to 10°C for several minutes.

10 The melt-drops turned into viscous, sticky liquid, solid particles did not form.

Trial 2:

Same procedure as above but now finely divided solid CN powder was added to the melt before setting the droplets on the plate. Solids of NH-CN and crushed CN*4H₂O crystals
15 were applied.

The melt-droplets turned into slurries with no particle strength as they cooled down.

Trial 3:

20 CN melt having 23 weight % water and 77 weight % CN were allowed to cool on a plate for 48 hours at 20°C. A white solid material was formed during this time

Now clearly the melt had turned into a strong solid material over these hours and X-ray analysis showed that the material consisted of CN*2H₂O and CN 3*H₂O.

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However, the solidifying time was too long for a convenient particulation process.

Trial 4a:

30 Same procedure as in trial 1, but now a CN-melt consisting of 23 weight % water and 77 weight % CN was cooled down to 50-55°C and 2 weight % crushed material from trial 3 was thoroughly mixed into the melt.

As the drops cooled, crystals were formed and during 30-70 second hard pastilles were formed with particle strength above 1 kg. As time passed, particle strength became substantially higher.

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Particles did form with this procedure and the crucial part of this procedure was obviously to add finely divided solid material consisting of the equilibrium phases of the system at room temperature ($\text{CN} \cdot 2\text{H}_2\text{O}$ and $\text{CN} \cdot 3\text{H}_2\text{O}$).

10 **Trial 4b:**

Same procedure as trial 4a but now melt composition was 25 weight % / 75 weight % and 21.5 weight % / 78,5 weight % ($\text{H}_2\text{O}/\text{CaN}$).

Trial 5:

15 Same procedure as in Trial 4, after reducing the temperature of the melt (23% weight % $\text{H}_2\text{O}/77\%$ weight % CN) to approximately 45°C the finely divided solid material was mixed in as seeding particles. As crystals started to form in the beaker, drops were allowed to fall on the cooling plate and simultaneously pure melt (23 weight % / 77 weight %) with temperature below 50°C was added to the beaker, while stirring.

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In this way drops containing solid crystals with the right composition were continuously formed and solidified on the metal plate just by adding one portion of solid material to make the crystallization start.

25 However, 40-70 seconds are too long time for using a granulation or prilling technique with an acceptable recycling ratio.

To use procedure 5 for producing large quantities of particles, a way of obtaining 40-70 second crystallization time was looked for.

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Example 4 – Making CN pastilles in industrial scale

Experiments were carried out on a moving steel cooling belt (as described in US patent No. 5326541) that is kept at a low temperature by using water as cooling agent. On this
5 belt a rotating drum with nozzles, supply drops that can solidify on the belt. A plant test was carried out with CN melt (23 weight %/ 77 weight %).

By using procedure described in "Trial 5", several hundred kg of CN particles (pastilles) were produced on the cooling belt.

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Example 5 – Making MgN pastilles

Trial 5 in Example 3 was repeated by replacing CN melt with 1: MgN-water melt having composition 67 weight % MgN and 33 weight % H₂O (boiling point 180 °C) and 2: MgN-water melt with composition 58 weight % MgN and 42 weight % (boiling point 155°C).
15 Both melt 1 and 2 were cooled down to 30°C by procedure mentioned in trial 5 (Example 3). Letting composition 1 and 2 solidify in an exsiccator for 3 days, and then crush the solids formed into a fine powder made seeding material.

With melt 1 and 2 and the procedure described we obtained MgN*4H₂O and MgN *6H₂O
20 respectively. MgN*6H₂O was made also without seeding material as the MgN*6H₂O melt very easily solidified.

Example 6 – Making pastilles of MgN-AN and CN

A melt consisting of 67 weight % CN, 4.0 weight % AN, 10 weight % MgN and 20
25 weight % water was held at 110°C. The melt was cooled down to 65°C and seeding material thoroughly mixed in as drops were allowed to fall on a cold metal plate.

During 60 seconds on the plate hard pastilles were formed. Letting the melt composition crystallize in an exsiccator for 2-3 days and then grinding to a fine powder made seeding
30 material.

Example 7 - Mixture of CN, AN and CaCl₂

A melt consisting of 50 weight % CN, 4 weight % AN, 26.5 weight % CaCl₂ and 18-20 weight % water was made by melting a mixture of NH-CN and CaCl₂*2H₂O (130-140°C).

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By using procedure described in 4 b (seeding material added at 120°C) nice particles were formed within 30 seconds on a cold steel plate. The particles consisted of homogenously solidified CaN-AN CaCl₂ particles.

Example 8 – Mixture of CN and KN

A melt consisting of 74 weight % CN, 14 weight % KN and 12 weight % water was made by evaporating water from a CN -KN -H₂O solution. The melt temperature was reduced to 86°C, app. 5-6°C above crystallization point. 3 weight % finely grained seed material was thoroughly mixed in and droplets allowed falling on to a cold metal plate (23°C).

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During 50-60 seconds hard pastilles/particles formed on the plate.

The right seeding material was made by letting the melt composition crystallise in an exsiccator over 2-3 days and then grind to powder the solid formed.

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Thus, by applying:

- correct melt or CN-water composition
- correct temperature of the melt (at or below cryst. point)
- correct seeding material (consists of equilibrium phases of the solidifying material)
- a cooling belt or a similar system that allows 20-70 seconds or more for crystallization,

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it has been possible to find a procedure for producing solid CN particles (CN+crystal water) without AN. The procedure can be applied for making solids of several nitrate systems containing Ca, Mg, K, Na, NH₄ or mixtures of these nitrates or mixtures of nitrates and chlorides.

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